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II. *A chemical Analysis of some Calamines.* By James Smithson,  
Esq. F. R. S.

Read November 18, 1802.

NOTWITHSTANDING the experiments of BERGMAN and others, on those ores of zinc which are called calamine, much uncertainty still subsisted on the subject of them. Their constitution was far from decided, nor was it ever determined whether all calamines were of the same species, or whether there were several kinds of them.

The Abbé HAUY, so justly celebrated for his great knowledge in crystallography and mineralogy, has adhered, in his late work,\* to the opinions he had before advanced,† that calamines were all of one species, and contained no carbonic acid, being a simple calx of zinc, attributing the effervescence which he found some of them to produce with acids, to an accidental admixture of carbonate of lime.

The following experiments were made to obtain a more certain knowledge of these ores; and their results will show the necessity there was for their farther investigation, and how wide from the truth have been the opinions adopted concerning them.

*Calamine from Bleyberg.*

a. The specimen which furnished the subject of this article,

\* *Traité de Mineralogie*, Tome IV.

† *Journal des Mines.*

was said by the German of whom it was purchased, to have come from the mines of Bleyberg in Carinthia.

It was in the form of a sheet stalactite, spread over small fragments of limestone. Its texture was not however at all crystalline, but of the dull earthy appearance of chalk, though, on comparison, of a finer grain and closer texture.

It was quite white, perfectly opaque, and adhered to the tongue; 68.0 grs. of it, in small bits, immersed in distilled water, absorbed 19.8 grs. of it, = 0.29.

It admitted of being scraped by the nail, though with some difficulty: scraped with a knife, it afforded no light.

68.1 grs. of it, broken into small pieces, expelled 19.0 grs. of distilled water from a stopple bottle. Hence its density = 3.584. In another trial, 18.96 grs. at a heat of 65° FAHRENHEIT, displaced 5.27 grs. of distilled water; hence the density = 3.598. The bits, in both cases, were entirely penetrated with water.

*b.* Subjected to the action of the blowpipe on the coal, it became yellow the moment it was heated, but recovered its pristine whiteness on being let cool. This quality, of temporarily changing their colour by heat, is common to most, if not all, metallic oxides; the white growing yellow, the yellow red, the red black.

Urged with the blue flame, it became extremely friable; spread yellow flowers on the coal; and, on continuing the fire no very long time, entirely exhaled. If the flame was directed against the flowers, which had settled on the coal, they shone with a vivid light. A bit fixed to the end of a slip of glass, wasted nearly as quickly as on the coal.

It dissolved in borax and microcosmic salt, with a slight

effervescence, and yielded clear colourless glasses; but which became opaque on cooling, if over saturated. Carbonate of soda had not any action on it.

c. 68.0 grs. of this calamine dissolved in dilute vitriolic acid with a brisk effervescence, and emitted 9.2 grs. of carbonic acid. The solution was white and turbid, and on standing deposited a white powder, which, collected on a small filter of gauze paper, and welledulcorated and let dry, weighed only 0.86 gr. This sediment, tried at the blowpipe, melted first into an opaque white matter, and then partially reduced into lead. It was therefore, probably, a mixture of vitriol of lead and vitriol of lime.

The filtered solution, gently exhaled to dryness, and kept over a spirit-lamp till the water of crystallization of the salt and all superfluous vitriolic acid were driven off, afforded 96.7 grs. of perfectly dry, or *arid*,\* white salt. On re-solution in water, and crystallization, this saline matter proved to be wholly vitriol of zinc, excepting an inappretiable quantity of vitriol of lime in capillary crystals, due, without doubt, to a slight and accidental admixture of some portion of the calcareous fragments on which this calamine had been deposited. Pure martial prussiate of tartar, threw down a white precipitate from the solution of this salt.

In another experiment, 20.0 grs. of this calamine afforded 28.7 grs. of arid vitriol of zinc.

d. 10 grs. of this calamine were dissolved in pure marine acid, with heat. On cooling, small capillary crystals of muriate of lead formed in the solution. This solution was precipitated

\* *Dry*, as opposed to wet or damp, which are only degrees of each other, merely implies free from mechanically admixed water. *Arid*, may be appropriated to express the state of being devoid of combined water.

by carbonate of soda, and the filtered liquor let exhale slowly in the air; but it furnished only crystals of muriate of soda.

e. 10 grs. dissolved in acetous acid without leaving any residuum. By gentle evaporation, 20.3 grs. = 2.03, of acetite of zinc, in the usual hexagonal plates, were obtained. These crystals were permanent in the air, and no other kind of salt could be perceived amongst them.

Neither solution of vitriolated tartar, nor vitriolic acid, occasioned the slightest turbidness in the solution of these crystals, either immediately or on standing; a proof that the quantity of lime and lead in this solution, if any, was excessively minute.

f. A bit of this calamine, weighing 20.6 grs. being made red hot in a covered tobacco-pipe, became very brittle, dividing on the slightest touch into prisms, like those of starch, and lost 5.9 grs. of its weight = 0.286. After this, it dissolved slowly and difficultly in vitriolic acid, without any effervescence.

According to these experiments, this calamine consists of,

|               |   |   |   |              |
|---------------|---|---|---|--------------|
| Calx of zinc  | - | - | - | 0.714        |
| Carbonic acid | - | - | - | 0.135        |
| Water         | - | - | - | 0.151        |
|               |   |   |   | <hr/> 1.000. |

The carbonates of lime and lead in it are mere accidental admixtures, and in too small quantity to deserve notice.

### *Calamine from Somersetshire.*

a. This calamine came from Mendip Hills in Somersetshire.

It had a mammillated form; was of a dense crystalline texture; semitransparent at its edges, and in its small fragments; and upon the whole very similar, in its general appearance, to calcedony.

It was tinged, exteriorly, brown; but its interior colour was a greenish yellow.

It had considerable hardness; it admitted however of being scraped by a knife to a white powder.

56.8 grs. of it displaced 13.1 grs. of water, at a temperature of 65° FAHRENHEIT. Hence its density = 4.336.

b. Exposed to the blowpipe, it became opaque, more yellow, and friable; spread flowers on the coal, and consequently volatilized, but not with the rapidity of the foregoing kind from Bleyberg.

It dissolved in borax and microcosmic salt, with effervescence, yielding colourless glasses. Carbonate of soda had no action on it.

c. It dissolved in vitriolic acid with a brisk effervescence; and 67.9 grs. of it emitted 24.5 grs. = 0.360, of carbonic acid. This solution was colourless; and no residuum was left. By evaporation, it afforded only vitriol of zinc, in pure limpid crystals.

d. 23.0 grs. in small bits, made red hot in a covered tobacco-pipe, lost 8.1 grs. = 0.352. It then dissolved slowly and difficultly in vitriolic acid, without any emission of carbonic acid; and, on gently exhaling the solution, and heating the salt obtained, till the expulsion of all superabundant vitriolic acid and all water, 29.8 grs. of arid vitriol of zinc were obtained. This dry salt was wholly soluble again in water; and solution of pure martial prussiate of soda occasioned a white precipitate in it.

This calamine hence consists of,

|               |   |   |   |        |
|---------------|---|---|---|--------|
| Carbonic acid | - | - | - | 0.352  |
| Calx of zinc  | - | - | - | 0.648  |
|               |   |   |   | <hr/>  |
|               |   |   |   | 1.000. |

*Calamine from Derbyshire.*

a. This calamine consisted of a number of small crystals, about the size of tobacco-seeds, of a pale yellow colour, which appeared, from the shape of the mass of them, to have been deposited on the surface of crystals of carbonate of lime, of the form of Fig. 28. Plate IV. of the *Cristallographie* of ROME' DE L'ISLE.

The smallness of these calamine crystals, and a want of sharpness, rendered it impossible to determine their form with certainty; they were evidently, however, rhomboids, whose faces were very nearly, if not quite, rectangular, and which were incomplete along their six intermediate edges, apparently like Fig. 78. Plate IV. of ROME' DE L'ISLE.

22.1 grs. of these crystals, at a heat of  $57^{\circ}$  FAHRENHEIT, displaced 5.1 grs. of water, which gives their density = 4.333.

Heat did not excite any electricity in these crystals.

b. Before the blowpipe, they grew more yellow and opaque, and spread flowers on the coal. They dissolved wholly in borax and microcosmic salt, with effervescence.

c. 22.0 grs. during their solution in vitriolic acid, effervesced, and lost 7.8 grs. of carbonic acid = 0.354. This solution was colourless, and afforded 26.8 grs. of arid vitriol of zinc, which, redissolved in water, shot wholly into clear colourless prisms of this salt.

d. 9.2 grs. of these crystals, ignited in a covered tobacco-pipe, lost 3.2 grs. = 0.3478; hence, these crystals consist of,

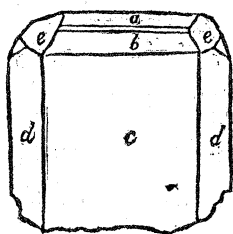
|               |   |   |   |              |
|---------------|---|---|---|--------------|
| Carbonic acid | - | - | - | 0.348        |
| Calx of zinc  | - | - | - | 0.652        |
|               |   |   |   | <hr/> 1.000. |

*Electrical Calamine.*

The Abbé HAUY has considered this kind as differing from the other calamines only in the circumstance of being in distinct crystals; but it has already appeared, in the instance of the Derbyshire calamine, that all crystals of calamine are not electric by heat, and hence, that it is not merely to being in this state that this species owes the above quality. And the following experiments, on some crystals of electric calamine from Regbania in Hungary, can leave no doubt of its being a combination of calx of zinc with quartz; since the quantity of quartz obtained, and the perfect regularity and transparency of these crystals, make it impossible to suppose it a foreign admixture in them.

a. 23.45 grs. of these Regbania crystals, displaced 6.8 grs. of distilled water, from a stopple-bottle, at the temperature of  $64^{\circ}$  FAHRENHEIT; their specific gravity is therefore = 3.434.

The form of these crystals is represented in the annexed Figure.



$$ac = 90^{\circ}.$$

$$ae = 150^{\circ}.$$

$$bc = 115^{\circ}.$$

$$cd = 130^{\circ}.$$

They were not scratched by a pin; a knife marked them.



b. One of these crystals, exposed to the flame of the blow-pipe, decrepitated and became opaque, and shone with a green light, but seemed totally infusible.

Borax and microcosmic salt dissolved these crystals, without any effervescence, producing clear colourless glasses. Carbonate of soda had little if any action on them.

c. According to Mr. PELLETIER's experiments\* on the calamine of Fribourg in Brigaw, which is undoubtedly of this species, its composition is,

|              |   |   |   |             |
|--------------|---|---|---|-------------|
| Quartz       | - | - | - | 0.50        |
| Calx of zinc | - | - | - | 0.38        |
| Water        | - | - | - | 0.12        |
|              |   |   |   | <hr/> 1.00. |

The experiments on the Regbania crystals have had different results; but, though made on much smaller quantities, they will perhaps not be found, on repetition, less in conformity with nature.

23.45 grs. heated red hot in a covered crucible, decrepitated a little, and became opaque, and lost 1.05 gr. but did not fall to powder or grow friable. It was found, that this matter was not in the least deprived of its electrical quality by being ignited; and hence, while hot, the fragments of these decrepitated crystals clung together, and to the crucible.

d. 22.2 grs. of these decrepitated crystals, = 23.24 grs. of the original crystals, in a state of impalpable powder, being digested over a spirit-lamp with diluted vitriolic acid, showed no effervescence; and, after some time, the mixture became a jelly. Exhaled to dryness, and ignited slightly, to expel the superfluous vitriolic acid, the mass weighed 37.5 grs.

\* *Journal de Physique*, Tome XX. p. 424.

On extraction of the saline part by distilled water, a fine powder remained, which, after ignition, weighed 5.8 grs. and was quartz.

The saline solution afforded, on crystallization, only vitriol of zinc.

These crystals therefore consist of,

|              |   |   |   |   |               |
|--------------|---|---|---|---|---------------|
| Quartz       | - | - | - | - | 0.250         |
| Calx of zinc | - | - | - | - | 0.683         |
| Water        | - | - | - | - | 0.044         |
|              |   |   |   |   | <u>0.977</u>  |
| Loss         | - | - | - | - | 0.023         |
|              |   |   |   |   | <u>1.000.</u> |

The water is most probably not an essential element of this calamine, or in it in the state of, what is improperly called, water of crystallization, but rather exists in the crystals in fluid drops interposed between their plates, as it often is in crystals of nitre, of quartz, &c. Its small quantity, and the crystals not falling to powder on its expulsion, but retaining almost perfectly their original solidity, and spathose appearance in the places of fracture, and, above all, preserving their electrical quality wholly unimpaired, which would hardly be the case after the loss of a real element of their constitution, seem to warrant this opinion.

If the water is only accidental in this calamine, its composition, from the above experiments, will be,

|              |   |   |   |   |               |
|--------------|---|---|---|---|---------------|
| Quartz       | - | - | - | - | 0.261         |
| Calx of zinc | - | - | - | - | 0.739         |
|              |   |   |   |   | <u>1.000.</u> |

I have found this species of calamine amongst the productions of Derbyshire, in small brown crystals, deposited, together with

the foregoing small crystals of carbonate of zinc, on crystals of carbonate of lime. Their form seems, as far as their minuteness and compression together would allow of judging, nearly or quite the same as that of those from Regbania; and the least atom of them immediately evinces its nature, on being heated, by the strong electricity it acquires. On their solution in acids, they leave quartz.

### OBSERVATIONS.

Chemistry is yet so new a science, what we know of it bears so small a proportion to what we are ignorant of, our knowledge in every department of it is so incomplete, so broken, consisting so entirely of isolated points thinly scattered like lucid specks on a vast field of darkness, that no researches can be undertaken without producing some facts, leading to some consequences, which extend beyond the boundaries of their immediate object.

1. The foregoing experiments throw light on the proportions in which its elements exist in vitriol of zinc. 23.0 grs. of the Mendip Hill calamine, produced 29.8 grs. of arid vitriol of zinc. These 23.0 grs. of calamine contained 14.9 grs. of calx of zinc; hence, this metallic salt, in an arid state, consists of *exactly equal* parts of calx of zinc and vitriolic acid.

This inference is corroborated by the results of the other experiments: 68.0 grs. of the Bleyberg calamine, containing 48.6 grs. of calx of zinc, yielded 96.7 grs. of arid vitriol of zinc; and, in another trial, 20.0 grs. of this ore, containing 14.2 grs. of calx of zinc, produced 28.7 grs. of arid vitriol of zinc. The mean of these two cases, is 62.7 grs. of arid vitriol of zinc, from 31.4 grs. of calx of zinc.

In the experiment with the crystals of carbonate of zinc from Derbyshire, 14.35 grs. of calx of zinc furnished indeed only 26.8 grs. of arid vitriol of zinc; a deficiency of about  $\frac{6}{100}$ , occasioned probably by some small inaccuracy of manipulation.

2. When the simplicity found in all those parts of nature which are sufficiently known to discover it is considered, it appears improbable that the proximate constituent parts of bodies should be united in them, in the very remote relations to each other in which analyses generally indicate them; and, an attention to the subject has led me to the opinion that such is in fact not the case, but that, on the contrary, they are universally, as appears here with respect to arid vitriol of zinc, fractions of the compound of very low denominators. Possibly in few cases exceeding five.

The success which has appeared to attend some attempts to apply this theory, and amongst others, to the compositions of some of the substances above analysed, and especially to the calamine from Bleyberg, induces me to venture to dwell here a little on this subject, and state the composition of this calamine which results from the system, as, besides contributing perhaps to throw some light on the true nature of this ore, it may be the means likewise of presenting the theory under circumstances of agreement with experiment, which, from the surprising degree of nearness, and the trying complexity of the case, may seem to entitle it to some attention.

From this calamine, containing, according to the results of the experiments on the Mendip Hill kind, too small a quantity of carbonic acid to saturate the whole of the calx of zinc in it, and from its containing much too large a portion of water to be in it in the state of mere moisture or dampness, it seems to

consist of two matters; carbonate of zinc, and a peculiar compound of zinc and water, which may be named *hydrate of zinc*.

By the results of the analysis of the Mendip Hill calamine, corrected by the theory, carbonate of zinc appears to consist of,

|               |   |   |   |                 |
|---------------|---|---|---|-----------------|
| Carbonic acid | - | - | - | $\frac{1}{3}$   |
| Calx of zinc  | - | - | - | $\frac{2}{3}$ . |

Deducting from the calx of zinc in the Bleyberg calamine, that portion which corresponds, on these principles, to its yield of carbonic acid, the remaining quantity of calx of zinc and water is in such proportions as to lead, from the theory, to consider hydrate of zinc as composed of

|                      |   |   |   |                 |
|----------------------|---|---|---|-----------------|
| Calx of zinc         | - | - | - | $\frac{3}{4}$   |
| Water, or rather ice | - | - | - | $\frac{1}{4}$ . |

And, from these results, corrected by the theory, I consider Bleyberg calamine as consisting of,

|                   |   |   |   |                 |
|-------------------|---|---|---|-----------------|
| Carbonate of zinc | - | - | - | $\frac{2}{5}$   |
| Hydrate of zinc   | - | - | - | $\frac{3}{5}$ . |

The test of this hypothesis, is in the quantities of the remote elements which analysis would obtain from a calamine thus composed.

The following table will show how very insignificantly the calamine compounded by the theory, would differ in this respect from the calamine of nature.

1000 parts of the compound salt of carbonate and hydrate of zinc consist of,

$$\begin{array}{rcl}
 \text{Carbonate of zinc } 400 = & \left\{ \begin{array}{l} \text{Carbonic acid} = \frac{400}{3} = - - - 133\frac{1}{3} \\ \text{Calx of zinc} = \frac{400 \times 2}{3} = 266\frac{2}{3} \end{array} \right\} & = - 716\frac{2}{3} \\
 \text{Hydrate of zinc } = 600 & \left\{ \begin{array}{l} \text{Calx of zinc} = \frac{600 \times 3}{4} = 450 \\ \text{Ice} - - = \frac{600}{4} = - - - 150 \end{array} \right\} & \\
 & & \hline
 & & 1000.
 \end{array}$$

Great as is the agreement between the quantities of the last column and those obtained by the analysis of the Bleyberg calamine, (page 15,) it would be yet more perfect, probably, had there been, in this instance, no sources of fallacy but those attached to chemical operations, such as errors of weighing, waste, &c. but the differences which exist are owing, in some measure at least, to the admixture of carbonate of lime and carbonate of lead, in the calamine analysed, and also to some portion of water, which is undoubtedly contained, in the state of moisture, in so porous and bibulous a body.

It has also appeared, in the experiments on the Mendip Hill calamine, that acids indicate a greater quantity of carbonic acid than fire does, by  $\frac{22}{1000}$ . If we make this deduction for dissolved water, it reduces the quantity of carbonic acid in the Bleyberg calamine, to 0.1321.

If we assume this quantity of carbonic acid as the datum to calculate, on this system, the composition of the calamine from Bleyberg, we shall obtain the following results :

|   |              |
|---|--------------|
| Compound salt, of carbonate of zinc and hydrate of zinc | 990.3        |
| Water, in the state of moisture                         | - - 2.5      |
| Carbonate of zinc and carbonate of lead                 | - - 7.2      |
|   | <hr/> 1000.0 |

It may be thought some corroboration of the system here offered, that, if we admit the proportions which it indicates, the remote elements of this ore, while they are regular parts of their immediate products, by whose subsequent union this ore is engendered, are also regular fractions of the ore itself: thus,

|                   |       |                   |
|-------------------|-------|-------------------|
| The carbonic acid | - - - | $= \frac{8}{60}$  |
| The water         | - - - | $= \frac{9}{60}$  |
| The calx of zinc  | - - - | $= \frac{43}{60}$ |

Hereby displaying that sort of regularity, in every point of view of the object, which so wonderfully characterises the works of nature, when beheld in their true light.

If this calamine does consist of carbonate of zinc and hydrate of zinc, in the regular proportions above supposed, little doubt can exist of its being a true chemical combination of these two matters, and not merely a mechanical mixture of them in a pulverulent state; and, if so, we may indulge the hope of some day meeting with this ore in regular crystals.

If the theory here advanced has any foundation in truth, the discovery will introduce a degree of rigorous accuracy and certainty into chemistry, of which this science was thought to be ever incapable, by enabling the chemist, like the geometrician, to rectify by calculation the unavoidable errors of his manual operations, and by authorising him to discriminate from the essential elements of a compound, those products of its analysis whose quantity cannot be reduced to any admissible proportion.

A certain knowledge of the exact proportions of the constituent

principles of bodies, may likewise open to our view harmonious analogies between the constitutions of related objects, general laws, &c. which at present totally escape us. In short, if it is founded in truth, its enabling the application of mathematics to chemistry, cannot but be productive of material results.\*

3. By the application of the foregoing theory to the experiments on the electrical calamine, its elements will appear to be,

|              |   |   |   |               |
|--------------|---|---|---|---------------|
| Quartz       | - | - | - | $\frac{1}{4}$ |
| Calx of zinc | - | - | - | $\frac{3}{4}$ |

A small quantity of the calamine having escaped the action of the vitriolic acid, and remained undecomposed, will account for the slight excess in the weight of the quartz.

4. The exhalation of these calamines at the blowpipe, and the flowers which they diffuse round them on the coal, are probably not to be attributed to a direct volatilization of them. It is more probable that they are the consequences of the dis-oxidation of the zinc calx, by the coal and the inflammable matter of the flame, its sublimation in a metallic state, and instantaneous recalcination. And this alternate reduction and combustion, may explain the peculiar phosphoric appearance exhibited by calces of zinc at the blowpipe.

The apparent sublimation of the common flowers of zinc at the instant of their production, though totally unsublimable afterwards, is certainly likewise but a deceptive appearance. The reguline zinc, vaporized by the heat, rises from the crucible as a metallic gas, and is, while in this state, converted to a calx. The flame which attends the process is a proof of it; for flame is a mass of vapour, ignited by the production of fire within itself.

\* It may be proper to say, that the experiments have been stated *precisely* as they turned out, and have not been in the *least degree* bent to the system.



The fibrous form of the flowers of zinc, is owing to a crystallization of the calx while in *mechanical suspension* in the air, like that which takes place with camphor, when, after having been some time inflamed, it is blown out.

A moment's reflection must evince, how injudicious is the common opinion, of crystallization requiring a state of solution in the matter ; since it must be evident, that while solution subsists, as long as a quantity of fluid admitting of it is present, no crystallization can take place. The only requisite for this operation, is a freedom of motion in the masses which tend to unite, which allows them to yield to the impulse which propels them together, and to obey that sort of polarity which occasions them to present to each other the parts adapted to mutual union. No state so completely affords these conditions as that of mechanical suspension in a fluid whose density is so great, relatively to their size, as to oppose such resistance to their descent in it as to occasion their mutual attraction to become a power superior to their force of gravitation. It is in these circumstances that the atoms of matters find themselves, when, on the separation from them of the portion of fluid by which they were dissolved, they are abandoned in a disengaged state in the bosom of a solution ; and hence it is in saturated solutions sustaining evaporation, or equivalent cooling, and free from any perturbing motion, that regular crystallization is usually effected.

But those who are familiar with chemical operations, know the sort of agglutination which happens between the particles of subsided very fine precipitates ; occasioning them, on a second diffusion through the fluid, to settle again much more quickly than before, and which is certainly a crystallization, but under circumstances very unfavourable to its perfect performance.

5. No calamine has yet occurred to me which was a real, uncombined, calx of zinc. If such, as a native product, should ever be met with in any of the still unexplored parts of the earth, or exist amongst the unscrutinized possessions of any cabinet, it will easily be known, by producing a quantity of arid vitriol of zinc exactly double its own weight; while the hydrate of zinc, should it be found single, or uncombined with the carbonate, will yield, it is evident, 1.5 its weight of this arid salt.